Slow crack propagation in polyethylene: determination and prediction

Witold Brostow*
Institut für Physikalische Chemie, Johannes-Gutenberg-Universität, D-6500 Mainz, Federal Republic of Germany

Manfred Fleissner
Polymerphysik, Hoechst AG, D-6230 Frankfurt am Main 80, Federal Republic of Germany

and Willi F. Müller
Anwendungstechnische Abteilung Kunststoffe, Hoechst AG, D-6230 Frankfurt am Main 80, Federal Republic of Germany
(Received 20 November 1989; revised 12 February 1990; accepted 13 February 1990)

A model is developed connecting the stress intensity factor K_I with the propagation rate dh/dt of slow cracks. The model is based on the concept of the chain relaxation capability. Experimental K_I *versus* dh/dt data are reported for polyethylenes of varying molecular mass M, density ρ, initial notch length h_0 and at different stress levels σ. Predictions of the theory concerning the effect of each of these parameters on crack propagation are confirmed by the experimental results. In particular, the equation for K_I as a function of dh/dt does not contain h_0 nor σ. Experimental plots of K_I *versus* dh/dt for common M but different h_0 values coincide into a single curve. Also plots for specimens of the same class but subjected to different stress levels form a single curve.

(Keywords: polymeric materials; slow crack propagation; polyethylene; mechanical properties; stress intensity factor; chain relaxation capability)

INTRODUCTION

Failure of polymeric materials and components occurs often at relatively insignificant stress levels, far below the tensile strength. One class of reasons for this involves a variety of environmental effects producing structural changes: penetration of liquid and vapour condensates into the material, irradiation from Sun or other light sources, nuclear radiation, and so on. The second class of reasons is related to the presence of flaws, inclusions and other stress concentrators in the material, typically introduced during processing, which in service can grow and result in shear bands, crazes and cracks. In this paper we are concerned with the most dangerous kind of flaws, namely cracks, and with their behaviour as a function of time.

Two key problems exist here. The first, that of rapid crack propagation (RCP), was studied in an earlier paper[1]; a quantitative criterion was developed enabling the prediction of RCP occurrence. In the present work we deal with the second and much more frequent problem of *slow* crack propagation. Polyethylene (PE) specimens were tested in tension under constant loads at a constant temperature; this was done in a water medium, which assured good temperature uniformity. The stress intensity factor K_I was determined as a function of the crack propagation rate dh/dt, where h denotes the crack depth and t time. Molecular mass M, sample density ρ, initial notch length h_0 and stress level σ were varied in turn.

Quantitative predictions of crack propagation in terms of the parameters named above involve the use of fracture mechanics (FM). FM was developed first for metals; connectedness of atoms in polymeric chains is not taken into account at all. Hence FM deals in a natural way with elasticity and plasticity rather than with viscoelasticity. At the same time, it is possible to deal simultaneously with more than one class of materials – provided interactions are properly taken into account. For instance, Kubát and collaborators[2–5] developed a cooperative theory of flow, leading to stress relaxation relations. While derived for polymers, the theory provides a relation applicable also with good results to metals. As another example, fracture-mechanical stress concentration factor contains essential characteristics of destructive processes occurring in polymers on impact. Simultaneously, non-destructive processes are characterized by the chain relaxation capability[6] (*CRC*; in German, die Kettenrelaxationsfähigkeit = *KRF*), which is related to free volume v^f and to the temperature shift factor a_T. Competition between these two classes of processes is the basis of a model of impact behaviour[7]; the theory connects stress concentration factors with impact transition temperatures. Predictions for low-density PE give satisfactory results. Conversely, v^f and polymer density can be calculated from impact data[8].

In the present work we again take advantage of fracture mechanics in conjunction with the concept of chain relaxation capability. We develop a model first. Then,

* Present address and to whom correspondence should be addressed: Center for Materials Characterization and Department of Chemistry, University of North Texas, Denton, TX 76203-5371, USA

0032-3861/91/030419-07

we report experimental results obtained following a procedure devised by one of us[9]. Finally, model predictions are compared with the experimental findings.

THEORY

The starting point is the definition of the stress intensity factor; see for instance a lucid review of FM by Pascoe[10] or an article by Provan[11]:

$$K_I = \alpha^* \pi^{1/2} \sigma h^{1/2} \quad (1)$$

K_I is the stress intensity factor, which characterizes the stress distribution field near the crack tip, with the index I referring to the opening or tensile mode of crack extension; α^* is a geometric factor appropriate to the particular crack and component shape; σ is the stress level; and h is the length or depth of the crack. The growth of the crack is characterized by the time derivative dh/dt. Of particular interest is the connection between K_I and the rate dh/dt. As noted also by Pascoe, the stress intensity factor should not be confused with the stress concentration factor; traditionally, both have not only similar names but also are represented by similar symbols.

FM provides us also with the Griffith equation (e.g. see again Pascoe[9]):

$$\sigma_{cr} = (2\Gamma E/\pi h)^{1/2} \quad (2)$$

Here σ_{cr} is the critical stress above which crack propagation occurs for given surface energy per unit area Γ and Young's modulus E. Equation (2) is applicable to the linear-elastic case in a straightforward manner. In view of earlier work and the discussion in the Introduction, we assume that the relation is applicable also to polymeric materials, but with appropriate definitions of the parameters. We recall[6] that *CRC* is equal to the amount of external energy dissipated by relaxation per unit time per unit weight of the polymer. Relaxation includes here conformational changes, segment vibrations transmitted along a given chain as well as to neighbouring chains, and also elastic energy storage resulting from bond stretching and angle changes. Clearly, average *CRC* in the material is different from a local value around the crack tip. The critical stress for propagation σ_{cr} involves factors producing local *CRC*, as well as long-range ones. As for local behaviour, we recall the theory of plastic flow of Argon[12,13] involving an analysis of local chain alignment. The long-range role is played by tie molecules, which prevent brittle slow crack fracture; the problem was analysed by Lustiger and his colleagues[14–16]. Moreover, we know that crazes play a role in crack propagation, a topic reviewed for instance by Kausch[17,18]. A transition from crazing to shear deformation caused by an increase in network strand density was demonstrated by Kramer and collaborators[19,20] for homopolymers, copolymers and blends. The strand is a portion of a chain bounded by entanglements or crosslinks. Entanglements are also important in fatigue crack propagation. Hertzberg[21] notes that their role becomes larger with an increase in molecular mass. Thus, Γ represents several factors; for a crack to propagate, energy has to be furnished for these various dissipative processes *plus* the energy necessary to break primary chemical bonds. Γ contains more than the critical energy release rate G_c (refs. 10, 11) and we recall that the latter was basically defined for brittle materials. We could have worked with the J-integral, but that would require additional assumptions. Finally, we note important work of Döll, Könczöl and Schinker[22] on crack propagation in fatigue loading; they established that the modulus E is a constant, independent of crack speed. Hence, the entire product $2\Gamma E$ in equation (2) is a material property.

Information pertinent for the significance of our σ_{cr} and Γ at the molecular level comes from computer simulations[23–25]. Under load, when a primary chemical bond such as C–C is broken, the adjacent polymer segments perform oscillations, with the amplitude decreasing with time. Segments further away from the broken bond perform similar but smaller oscillations. If the amount of free volume in the material is low, the oscillation frequency is high, as well as vice versa[24]. After some time, the oscillations subside; the segment finds for itself a new location consistent with the forces applied. Clearly, such oscillations provide a contribution to *CRC*. In stress–strain simulations[25] in which a double-well potential enables conformational changes, the plateau of the diagram corresponds to a large number of conversions of the *gauche–trans* type. When the number of conversions that are still possible becomes low, the plateau ends.

Apart from the molecular dynamics simulations, conformational transitions can be studied in terms of the internal orientational autocorrelation function (*OACF*). Bahar and Erman[26] evaluated *OACF* for a complete set of transitions between conformers by using a scheme of Jernigan[27]. They conclude that there exists only a *single* value of activation energy for transitions in carbon chains, regardless of sequence size and constraints due to chain connectivity. In addition to all of the above, creating new surfaces during crack propagation is of course determined mainly by breaking primary chemical bonds such as C–C, not unlike breaking metallic or ionic bonds in non-viscoelastic materials. Thus, both σ_{cr} and Γ depend on the same set of factors for a viscoelastic material; and both reduce to the quantities originally defined by FM for the linear-elastic case.

We are now in a position to ask a different question: For a given imposed stress σ, what is the critical crack length h_{cr} above which crack propagation will occur? Of course, h_{cr} so defined is independent of time. In other words, equation (2) is concerned with the situation when for a given material (given Γ and E) and given crack length h we increase the stress until crack propagation occurs at σ_{cr}. Now we consider an inverse situation when the stress level is fixed while we increase the notch length until crack propagation occurs at a value to be denoted by h_{cr}. In analogy to equation (2) generalized to include chain systems, we now write:

$$h_{cr} = 2\Gamma E/\pi\sigma^2 \quad (3)$$

In view of equation (3), when crack propagation does occur, its rate dh/dt should be related to the excess of the crack length at any given time $h(t)$ over the critical length. The already mentioned molecular dynamics simulations produce crack propagation in certain cases; a crossover exists from the region dominated by chain relaxation to the other region in which crack propagation does occur[24]. One also recalls an analysis by Kubát[3] of elementary events (transitions) accumulating to produce a macroscopic process. We assume a direct proportionality:

$$dh/dt = \beta(h - h_{cr}) \qquad \text{when } h \geqslant h_{cr} \quad (4)$$

Here β is a time-independent proportionality factor characteristic for the material, related to *CRC* and dependent on the applied stress σ.

We now denote $h(0)$ by h_0. Rearranging equation (4) and integrating we obtain:

$$h = h_{cr} + (h_0 - h_{cr})\,e^{\beta t} \tag{5}$$

an important result. The crack propagation rate is, therefore:

$$dh/dt = \beta(h_0 - h_{cr})\,e^{\beta t} \tag{6}$$

We can now connect the stress intensity factor, equation (1), with the crack growth. By using equations (5) and (3) we arrive at:

$$K_I = \alpha^*(2\Gamma E)^{1/2}[1 + (h_0/h_{cr} - 1)\,e^{\beta t}]^{1/2} \tag{7}$$

We see that in equation (7) the stress is represented by the critical crack length h_{cr}; the latter can be obtained from the former via equation (3). Thus, equation (7) tells us that the dependence of K_I on σ appears only in the time-dependent factor.

Inverting equation (7) and using equation (6), so as to have an explicit expression for the crack propagation rate, is also of interest:

$$dh/dt = \beta h_{cr}(K_I^2/\alpha^{*2}2\Gamma E - 1) \tag{8}$$

Except for K_I, all factors on the r.h.s. of equation (8) are time-independent.

Consider now a series of cases when we have specimens of a polymer of the same type, but differing in mass density ρ, that is in v^f. This at a constant temperature, so that the thermal energy is not affected, while typically the degree of crystallinity is. From the definition of the proportionality factor β, equation (4), we infer that β should decrease when *CRC* increases; under the same conditions h_{cr} should increase. Hence approximately:

$$CRC \sim v^f \sim \rho^{-1} \sim \beta^{-1} \sim h_{cr} \tag{9}$$

If the stress level and crack length have common values, that is all specimens have the same value of K_I, we find from proportionality (9) and equation (8) that the derivative dh/dt should go symbatically with polymer density.

Apart from the free volume, another parameter that should affect the relationship between K_I and dh/dt is the relative molecular mass M. In a study of fatigue crack propagation (FCP) of poly(vinyl chloride) (PVC), Hertzberg and collaborators[28,21] found a 1000-fold decrease in FCP rates when M of PVC increased approximately by a factor of 3. We know from the extensive work of Flory and others on the rotational isomeric state model of chain molecules how rapidly the partition function increases with the degree of polymerization, that is with M (see Ch. III in ref. 29; for a succinct review see Mattice[30]). Thus, because of conformational rearrangements as well as entanglements, *CRC* should increase along with molecular mass; for a constant K_I value but different M values, low dh/dt values will be associated with high M, as well as vice versa. Another important component of the relaxation is the transmission of energy along the chain, including exchange with neighbouring chains, and producing among others intensified vibrations of the segments. We know from a neutron scattering study of Fujara and Petry[31] over temperature ranges including the glass transition region that the frequency of vibrations does not change with T, but the amplitude does. As seen in molecular dynamics simulations[24], stress states affect the vibrations similarly as a temperature increase. Thus, conclusions reached on the basis of considerations of conformational changes, entanglements and vibrations are the same. On all these grounds:

$$M \sim CRC \sim \beta^{-1} \tag{10}$$

and at a fixed K_I an increase in M should bring about a decrease of the crack propagation rate.

In view of equation (7), we now return to equation (6) and obtain therefrom:

$$(1/\beta h_{cr})\,dh/dt = (h_0/h_{cr} - 1)\,e^{\beta t} \tag{11}$$

The last result substituted into equation (7) provides a convenient expression for K_I in terms of dh/dt. Since experimentalists customarily use logarithmic coordinates, we write:

$$\log K_I = \frac{1}{2}\log(\alpha^{*2}2\Gamma E) + \frac{1}{2}\log[1 + (1/\beta h_{cr})\,dh/dt] \tag{12}$$

We find from equation (6) that dh/dt depends on h_0, as indeed expected. Much less expected is another consequence of our model visible from equation (12): for specimens of the same material but different initial crack lengths, plots of K_I *versus* dh/dt should produce a common curve, independent of h_0.

Consider now a material to which a high value of stress has been applied. From the crack propagation rate formula, equation (4), we infer that β will be high also. At the same time, according to equation (3), h_{cr} will be low. The same argument applies also in reverse: low stress is connected with low β and high h_{cr}. Since β and h_{cr} vary in the opposite directions, if their variation rates are comparable, we should have:

$$\beta h_{cr} = c \tag{13}$$

so that c for a given material would be a constant independent of the stress level. It should be noted that equation (13) is not a direct consequence of the theory developed above which produced equation (12) but an additional assumption – albeit a plausible one. If equation (13) were true, plots of K_I *versus* dh/dt should be independent of the stress level. We shall find to what extent the main predictions of our model, as well as relation (13), are confirmed by the experimental results.

EXPERIMENTAL

We have studied PE homopolymers of medium molecular mass M, but several M values. Measurements of viscosity η were made in decahydronaphthalene at 135°C, in the same way as in an earlier study by one of us[32] of viscosity of PE melts and its relationship to the intrinsic viscosity $[\eta]$ of solutions. We have now obtained the Staudinger index (intrinsic viscosity) $[\eta]$; gel permeation chromatography has provided molecular mass distributions.

One PE sample, call it A, had $M_\eta = 9.0 \times 10^4$, $M_w/M_n \approx 5.5$, $[\eta] = 195\ cm^3\ g^{-1}$ and $\rho = 0.960\ g\ cm^{-3}$. Sample B has $M_\eta = 1.65 \times 10^5$, $M_w/M_n = 5.5$, $[\eta] = 295\ cm^3\ g^{-1}$ and $\rho = 0.955\ g\ cm^{-3}$. For sample C the values are, in the same order: 2.45×10^5, 5.5, $395\ cm^3\ g^{-1}$ and $0.951\ g\ cm^{-3}$.

Materials for testing in the form of sheets were obtained by compression moulding under identical conditions.

Tensile specimens, saw-cut from the sheets, with dimensions $70 \times 30 \times 4\ mm^3$, clamped length of 50 mm, were provided with a single-edge notch (SEN) each. Initial length of the notch h_0 was varied between 1.1 and 4.4 mm. Slow crack propagation was studied under tension in water at 60°C. Applied stresses varied between 0.7 and $2.1\ J\ cm^{-3}$ (advantages for working with this pressure unit are discussed in section 5.3 of ref. 33; $1\ J\ cm^{-3} = 1$ MPa).

The experimental set-up was such that crack propagation was easily followed laterally with a microscope. As noted elsewhere[9], already preliminary results had shown that the crack growth rate, dh/dt in our terminology, is governed by the stress intensity factor K_I. Values of K_I were computed from equation (1), with the geometric factor α^* calculated for the SEN case as prescribed by the ASTM[34].

RESULTS AND DISCUSSION

First of all, we note that experimental studies of slow crack growth are vastly different from those of rapid crack propagation. In RCP studies, changes in crack length with time are determined after a knife is pushed through a pressurized pipe by a falling weight[35,36,1], and velocities up to $400\ m\ s^{-1}$ were reported. In the present study, crack growth rates are lower by several orders of magnitude. Origins of slow cracks require further studies; presumably processing, subsequent transportation and handling, as well as environmental effects, are involved. Criens and Moslé[37] as well as Criens[38] provide recommendations for minimizing effects of knit lines in injection moulding. The recommendations make possible considerable reduction – but not complete elimination – of processing-introduced structural inhomogeneities.

Effects of molecular mass, that is results for samples A, B and C, are shown as K_I *versus* dh/dt curves in *Figure 1*. Full curves are calculated by using equation (12), points represent experimental values. The data for sample A, in part reported before[9], are the most extensive and include a number of stress levels, as well as a number of initial notch lengths h_0. For each curve, one kind of symbol, such as filled triangles, corresponds to a single value of h_0 and σ.

We now analyse the experimental results in terms of predictions from the theoretical model in the earlier section, qualitatively at first. The following observations are in order:

(i) At a constant level of the stress intensity factor, an increase in the chain length, that is in M, produces a decrease in the crack propagation rate. This is precisely what equation (8) in conjunction with the proportionality (10) have told us.

(ii) As predicted by equation (12), for a given class of specimens (common value of M) such as A, the initial crack length h_0 does not affect the K_I *versus* dh/dt relationship. Results for different h_0 values can be represented by a common curve virtually within the limits of experimental accuracy.

(iii) An additional conjecture from the model, equation (13), is also confirmed by the experimental results. Again within the limits of experimental accuracy, plots of K_I *versus* dh/dt for specimens of the same class but subjected to different stress levels can be represented by a single curve.

Calculations were made by using equation (12) for curves A, B, and C. The resulting values of $\alpha^*(2\Gamma E)^{1/2}$ are 1.01, 1.03 and $1.05\ J\ cm^{-5/2}$. Values of βh_{cr} are, respectively, 5.33×10^{-7}, 3.47×10^{-7} and 1.41×10^{-7}. The goodness of fit is represented by Δ, the root-mean-square deviations, 1.24×10^{-2}, 1.35×10^{-2} and 4.98×10^{-3}; and by the average percentage differences $\bar{D}$, 5.50, 4.50 and 1.86%. Here:

$$\bar{D} = \frac{100\%}{n} \sum_{i=1}^{n} \frac{|F_i^{exper} - F_i^{calc}|}{F_i^{exper}} \tag{14}$$

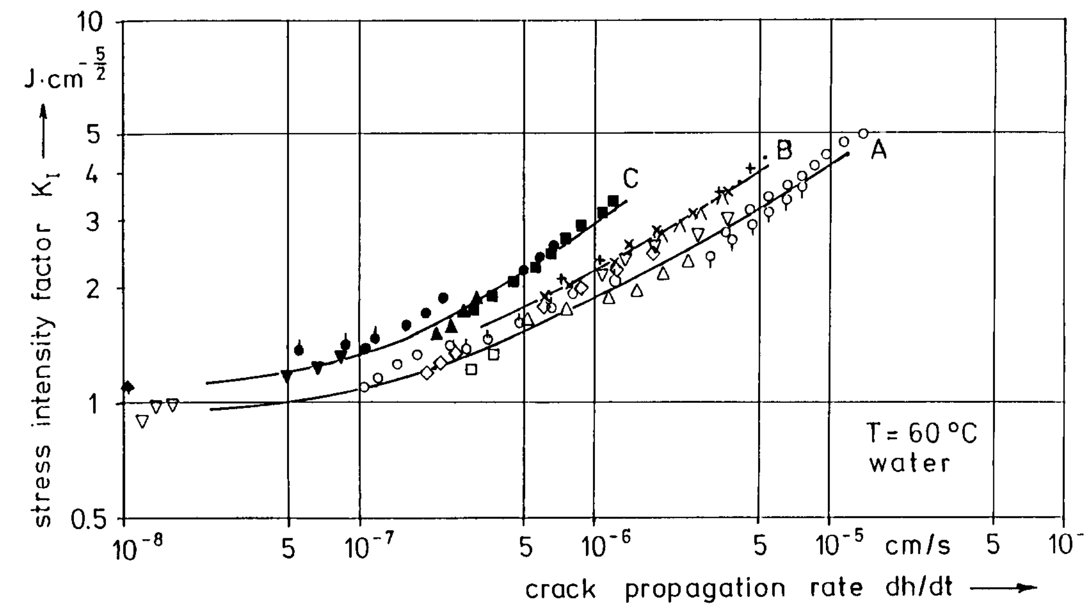

Figure 1 Stress intensity factor K_I as a function of crack propagation rate dh/dt for specimens of class A, B and C (see text) under uniaxial tension in water at 60°C. Full curves are calculated by using equation (12). Each kind of symbol pertains to a single value of σ and h_0. Thus, for curve A, the values of σ ($J\ cm^{-3}$) and h_0 (mm) are, respectively: 0.74 and 3.3 for ∇ in lower part of the curve; 1.07 and 2.3 for ○ in lower part of the curve; 1.24 and 2.0 for ◇; 1.26 and 2.15 for ȯ; 1.72 and 1.15 for □; 1.68 and 2.0 for Δ; 1.70 and 2.1 for ▿ in upper part of the curve; 1.69 and 4.35 for ○ in upper part of the curve; and 2.08 and 2.1 for ♀

Table 1 Properties of polymer samples and parameters of equation (12)

Code number	Density ρ (g cm^{-3})	VN (cm^3 g^{-1})	$[\eta]$ (cm^3 g^{-1})	M	$\alpha^*(2\Gamma E)^{1/2}$	βh_{cr}	Δ	$\bar{D}$ (%)
B1	0.9595	395	350	2.10×10^5	0.90	3.22×10^{-7}	3.75×10^{-2}	12.0
B3	0.9495	345	295	1.65×10^5	1.23	2.14×10^{-7}	1.85×10^{-2}	7.2
B6	0.9415	305	290	1.55×10^5	1.50	9.81×10^{-8}	0.98×10^{-2}	2.8
B7	0.9375	275	255	1.35×10^5	1.86	7.67×10^{-8}	3.05×10^{-2}	8.3

M_w/M_n for the sample B1 is 14 ± 4; for subsequent samples it goes down along with falling density

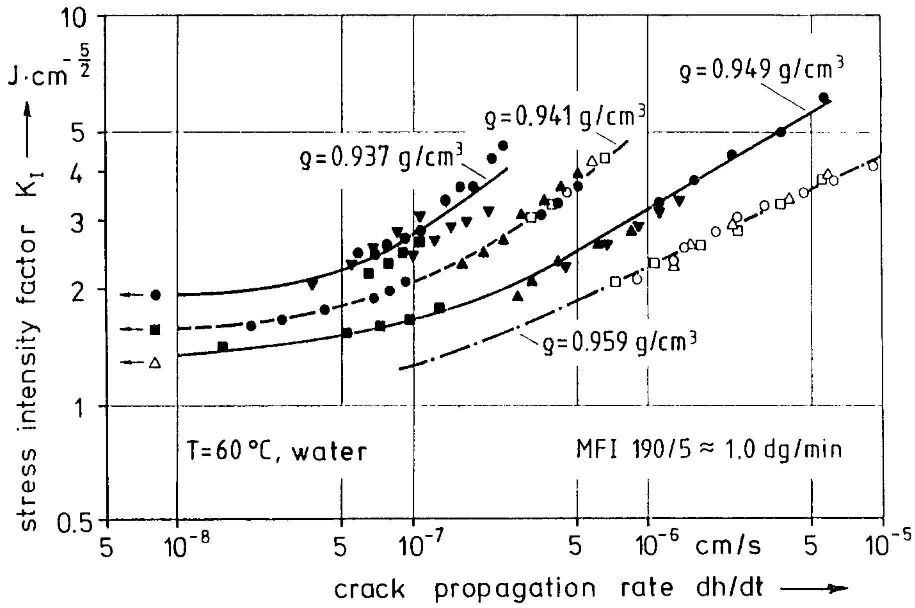

Figure 2 Stress intensity factor K_I as a function of crack propagation rate dh/dt for specimens of varying density. Uniaxial tension in water at 60°C. Full curves calculated from equation (12). Characteristics of the materials and parameters of equation (12) are provided in *Table 1*

and in our case $F = K_I$ and the index i runs over n experimental points. Thus, also:

(iv) Equation (12) represents the measured values within the limits of the experimental accuracy.

Experiments were also done to test the effect of polymer density. The series was prepared with a different catalyst, with M values also $\approx 10^5$, but a wider M distribution; one aimed here at maintaining the melt index approximately constant. The samples studied are characterized in *Table 1*. VN is the viscosity number, here the solution viscosity at $c = 1.0 \times 10^{-3}$ g cm^{-3}, related to the Staudinger index by the Martin equation[39]:

$$\log(VN) = \log[\eta] + 0.139[\eta]c \qquad (15)$$

The same table contains calculated values of the parameters of equation (12) as well as Δ and $\bar{D}$ characterizing the extent of agreement between calculation and experiment. In *Figure 2* we can see the experimental points as well as full curves calculated from equation (12).

The results in *Figure 2* agree with the findings for the series in which M was varied. Moreover:

(v) Moving horizontally in the diagram, that is maintaining K_I constant, we find that the crack propagation rate goes symbatically with the polymer density. This was predicted from our model, equation (8) in conjunction with proportionality (9).

From the results in *Figure 2* one can also determine values of K_I corresponding to the limit of dh/dt tending

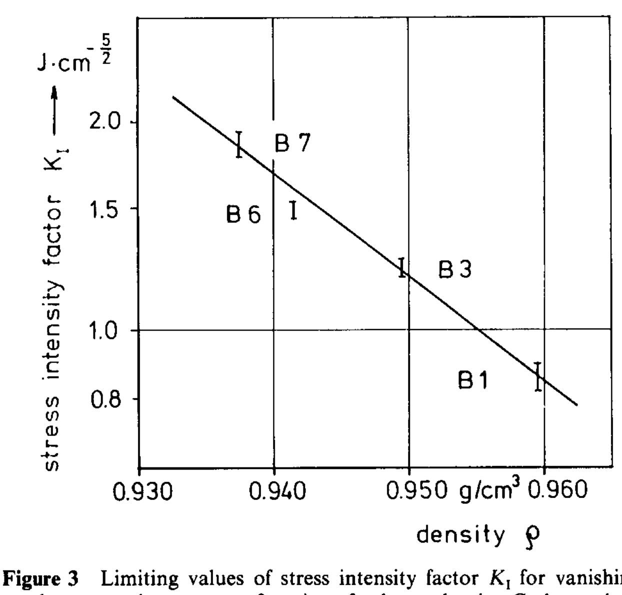

Figure 3 Limiting values of stress intensity factor K_I for vanishing crack propagation rates as a function of polymer density. Code numbers explained in *Table 1*

to zero. These values are presented graphically in *Figure 3*. From equation (8) we obtain

$$\lim_{dh/dt \to 0} K_I = \alpha^*(2\Gamma E)^{1/2} \qquad (16)$$

In molecular dynamics simulations referred to before[24] we have also seen how an increase in free volume enhances the amplitude of segment oscillations – as indeed was to be expected. Since oscillations dissipate mechanical energy, when v^f increases more energy is required for crack propagation, and our generalized Γ must be higher:

$$CRC \sim v^f \sim \Gamma \sim \rho^{-1} \tag{17}$$

The proportionality (17) resembles (10), except for the fact that Γ and β are inversely proportional, and that β depends on the stress level while Γ does not. Now relations (16) and (17) imply the direction of the change of lim K_I with density. From the results displayed in *Figure 3* we find that:

(vi) A prediction from equation (16) in conjunction with proportionality (17) is confirmed by the experiment: the limiting K_I values for vanishing crack propagation rates go down with increasing polymer density.

CONCLUDING REMARKS

The role of v^f constitutes a *leitmotif* in our considerations. We know how important free volume is for mechanical and rheological properties in general, due to work by Ferry[40], Holzmüller[41], Matsuoka[42,43], Kubát[2–5], Struik[44,45] and others. While we are discussing competition between *CRC* and destructive processes, with the *CRC* concept defined first in 1985[6], in 1986 Raab, Schulz and Pelzbauer[46] talked somewhat similarly about two competing mechanisms: orientational hardening and crack propagation. The statement that the stress intensity factor K_I controls the crack propagation rate dh/dt was made and analysed in some detail by Chan and Williams[47], and later also by others[48]. Some confusion on the validity of this statement resulted, apparently because Chan and Williams assumed that K_I is proportional to $(dh/dt)^n$. Consequently, various parts of K_I *versus* dh/dt curves seemed to show various values of the exponent n, and attempts were made to ascribe different process mechanisms to these parts. For instance, one assumed sharp crack propagation first, blunt crack afterwards, and a transition between these two regimes. There is, however, no basis for such a proportionality.

We find that the FM concepts, redefined by us so as to include effects other than linear elastic, serve well for prediction of slow crack propagation. This agrees with earlier work on applications of FM to polymeric materials. We recall the results of Kusy and collaborators[49,50] showing that the fracture surface energy varies with M. One expects that our approach should have ramifications to other aspects of mechanical behaviour of polymers. For instance, molecular factors that led us to the proportionality (10) are equally pertinent for the problem of impact resistance. Since the critical energy release rate G_c goes symbatically with *CRC*, G_c has to increase with M. This is what one of us has found[51] from measurements of the Charpy impact resistance of a variety of polyethylenes, with their structure characterized mainly by the Staudinger index. The same study[51] has shown that G_c decreases with increasing density. This last finding evidently follows from the first and the last members of proportionality (9).

An interesting study of creep and recovery of ultra-high-modulus PE was conducted by Wilding and Ward[52,53]. They report that the materials showed an apparent critical stress below which there was no detectable permanent creep. This of course fits well with the concept of *CRC* as well as with the results presented in this work. Wilding and Ward have found an exception, namely low-M homopolymers; in turn that result can be explained in conjunction with our proportionality (10), since *CRC* might not manifest itself if the chains are too short.

Highly pertinent for industry is the problem of creep rupture strength and ageing of plastic pipes[54–56], which apparently can be related to time to failure of specimens with a circumferential notch[9]. As enumerated in the previous section, all conclusions from our model of slow crack propagation, including the quantitative ones, are confirmed by experiment. This requires us to find quantitative relations replacing the present proportionalities (9), (10) and (17).

Since equation (13) has been confirmed by experiment, and since equation (12) contains as parameters two factors, $\alpha^*(2\Gamma E)^{1/2}$ and βh_{cr}, we would like to connect these factors to the chemical structure of the chains, free volume and *CRC*. Various measures of *CRC* are possible, but the temperature shift factor a_T pertaining to the time (t)–temperature (T) superposition was used with good results before[6–8]. As discussed by Hartmann[57], that principle is applicable also to the yield stress σ_y and yield energy E_y. In turn, σ_y is related to free volume v^f, or in particularly simple cases just to specific volume v[57,58]. This and proportionality (9) suggest the existence of a relationship between β, h_{cr}, v^f and σ_y. Since $v = v^* + v^f$, where v^* is the characteristic ('hard-core') volume, a formula for $v^f(T)$ is needed. A number of such relations exist, including the generalized Guggenheim formula[59] used before[8], and the Hartmann equation of state[60], which gives good results for both polymer solids[61] and liquids[62]. We expect to report a connection between the yield stress and the parameters of our crack propagation model in a later paper.

ACKNOWLEDGEMENTS

Various aspects of this work were discussed with a number of colleagues, including: Professor Wieslaw Binienda, University of Akron; Dr Ralf M. Criens, Central Research and Technology, Siemens AG, Munich; Professor Roger D. Corneliussen, Drexel University; Dr Bruce Hartmann, Polymer Physics Group, NSWC, Silver Spring, MD; Dr Zenon Joffe, Borg-Warner SA, Villers-Saint-Sépulcre, France; Dr Laszlo Könczöl, Frauenhofer Institute of Materials Mechanics, Freiburg i. Br.; Professor Josef Kubát, Chalmers University of Technology, Gothenburg, Sweden; and Dr Mannes Wolters, VEG Gas Institute, Apeldoorn, the Netherlands. One of us (W.B.) acknowledges also a Research Award of the Deutsche Forschungsgemeinschaft, Bonn, and a leave of absence from Drexel University in Philadelphia.

REFERENCES

1 Brostow, W. and Müller, W. F. *Polymer* 1986, **27**, 76
2 Högfors, Ch., Kubát, J. and Rigdahl, M. *Phys. Status Solidi* (*B*) 1981, **107**, 147
3 Kubát, J. *Phys. Status Solidi* (*B*) 1982, **111**, 599
4 For a review see Kubát, J. and Rigdahl, M. 'Failure of Plastics' (Eds. W. Brostow and R. D. Corneliussen), Hanser, Munich, 1986, Ch. 4

5 Ek, C. G., Kubát, J. and Rigdahl, M. *Colloid Polym. Sci.* 1987, **265**, 803
6 Brostow, W. *Mater. Chem. Phys.* 1985, **13**, 47
7 Brostow, W. 'Failure of Plastics' (Eds. W. Brostow and R. D. Corneliussen), Hanser, Munich, 1986, Ch. 10
8 Brostow, W. and Macip, M. A. *Macromolecules* 1989, **22**, 2761
9 Fleissner, M. *Kunststoffe – German Plastics* 1987, **77**, 45
10 Pascoe, K. J. 'Failure of Plastics' (Eds. W. Brostow and R. D. Corneliussen), Hanser, Munich, 1986, Ch. 7
11 Provan, J. W. *J. Mater. Educ.* 1988, **10**, 325
12 Argon, A. S. *Phil. Mag.* 1973, **28**, 839
13 Argon, A. S. and Bessonov, M. I. *Phil. Mag.* 1977, **35**, 917
14 Lustiger, A. and Markham, R. L. *Polymer* 1983, **24**, 1647
15 Lustiger, A. and Corneliussen, R. D. *J. Polym. Sci. Phys.* 1986, **24**, 1625
16 Lustiger, A. 'Failure of Plastics' (Eds. W. Brostow and R. D. Corneliussen), Hanser, Munich, 1986, Ch. 16
17 Kausch, H. H. 'Failure of Plastics' (Eds. W. Brostow and R. D. Corneliussen), Hanser, Munich, 1986, Ch. 5
18 Kausch, H. H. 'Polymer Fracture', 3rd Edn., Springer, Berlin, 1987
19 Berger, L. L. and Kramer, E. J. *J. Mater. Sci.* 1987, **22**, 2739
20 Berger, L. L. and Kramer, E. J. *J. Mater. Sci.* 1988, **23**, 3536
21 Hertzberg, R. W. 'Deformation and Fracture Mechanics of Engineering Materials', 2nd Edn., Wiley, New York, 1983
22 Döll, W., Könczöl, L. and Schinker, M. G. *Polymer* 1983, **24**, 1213
23 Cook, R. and Mercer, M. B. *Mater. Chem. Phys.* 1985, **12**, 571
24 Brostow, W. and Turner, D. P. *J. Rheol.* 1986, **30**, 767
25 Cook, R. *J. Polym. Sci. Phys.* 1987, **26**, 1337, 1349
26 Bahar, I. and Erman, B. *Macromolecules* 1987, **20**, 2310
27 Jernigan, R. L. 'Dielectric Properties of Polymers' (Ed. F. E. Karasz), Plenum, New York, 1972, p. 99
28 Rimnac, C. M., Manson, J. A., Hertzberg, R. W., Webler, S. M. and Skibo, M. D. *J. Macromol. Sci. Phys.* 1981, **19**, 351
29 Flory, P. J. 'Statistical Mechanics of Chain Molecules', Wiley-Interscience, New York, 1969
30 Mattice, W. L. *J. Mater. Educ.* 1982, **4**, 759
31 Fujara, F. and Petry, W. *Europhys. Lett.* 1987, **4**, 921
32 Fleissner, M. *Angew. Makromol. Chem.* 1981, **94**, 197
33 Brostow, W. 'Science of Materials', Wiley, New York, 1979; Brostow, W. 'Introductión a la ciencia de los materiales', Limusa, México, 1981; Brostow, W. 'Einstieg in die moderne Werkstoffwissenschaft', Hanser, Munich, 1985
34 Brown, W. F. and Srawley, J. E. ASTM STP 410, 1966
35 Gaube, E. and Müller, W. F. *Kunststoffe – German Plastics* 1980, **70**, 72
36 Gaube, E. and Müller, W. F. *Plastic Fuel Pipe Symp. Proc.* 1983, **8**, 133; Gaube, E. and Müller, W. F. *3R International* 1984, **23**, 236
37 Criens, R. M. and Moslé, H.-G. 'Failure of Plastics' (Eds. W. Brostow and R. D. Corneliussen), Hanser, Munich, 1986, Ch. 21
38 Criens, R. M. *Mater. Chem. Phys.* 1986, **14**, 69
39 Elliot, J. H., Horrowitz, K. H. and Hoodock, T. *J. Appl. Polym. Sci.* 1970, **14**, 2947
40 Ferry, J. D. 'Viscoelastic Properties of Polymers', 3rd Edn., Wiley, New York, 1980
41 Holzmüller, W. *Adv. Polym. Sci.* 1978, **26**, 1
42 Matsuoka, S. *J. Rheol.* 1986, **30**, 869
43 Matsuoka, S. 'Failure of Plastics' (Eds. W. Brostow and R. D. Corneliussen), Hanser, Munich, 1986, Ch. 3
44 Struik, L. C. E. 'Physical Aging in Amorphous Polymers and Other Materials', Elsevier, Amsterdam, 1978
45 Struik, L. C. E. 'Failure of Plastics' (Eds. W. Brostow and R. D. Corneliussen), Hanser, Munich, 1986, Ch. 11
46 Raab, M., Schulz, E. and Pelzbauer, Z. *Plaste Kautschuk* 1986, **33**, 341
47 Chan, M. K. V. and Williams, J. G. *Polymer* 1983, **24**, 234
48 Tonyali, K. and Brown, H. R. *J. Mater. Sci.* 1986, **21**, 3116
49 Kusy, R. P. and Turner, D. T. *Polymer* 1976, **17**, 161
50 Kusy, R. P. and Katz, M. J. *J. Mater. Sci.* 1976, **11**, 1475
51 Fleissner, M. *Angew. Makromol. Chem.* 1982, **105**, 167
52 Wilding, M. A. and Ward, I. M. *Polymer* 1978, **19**, 969
53 Wilding, M. A. and Ward, I. M. *Polymer* 1981, **22**, 870
54 Walters, M. and Scholten, F. L. *Proc. Plastic Fuel Gas Pipe Symp.* 1985, **9**, 91
55 Mruk, S. A. *Proc. Plastic Fuel Gas Pipe Symp.* 1985, **9**, 202
56 Gaube, E., Gebler, H., Müller, W. H. and Gondro, C. *Kunststoffe – German Plastics* 1985, **75**, 412
57 Hartmann, B. 'Encyclopedia of Engineering Materials' (Ed. N. P. Cheremisinoff), Marcel Dekker, New York, 1988, Vol. 2, Part A, Ch. 3
58 Hartmann, B., Lee, G. F. and Wong, W. *Polym. Eng. Sci.* 1987, **27**, 823
59 Ruether, J. A., Brostow, W. and Macip, M. A. *Mater. Chem. Phys.* 1986, **15**, 483
60 Hartmann, B. *Proc. Can. High Polymer Forum* 1983, **22**, 20
61 Hartmann, B. and Haque, M. A. *J. Appl. Polym. Sci.* 1985, **30**, 1553
62 Hartmann, B.and Haque, M. A. *J. Appl. Phys.* 1985, **58**, 2831